Sulphide oxidation Passivation technique

Boojum Research LTD: Collaborative Research with U of Toronto
University of Toronto
March to April 2009
By Carlos Paulo

TABLE OF CONTENTS

1. The concept

It is known that once exposed to an oxidizing environment (water or oxygen) as series of reactions occur at the surface of sulfide minerals, as pyrite, and lead to acid drainage generation.The major steps of pyrite oxidation are:

(1) Oxidation of sulfur in presence of atmospheric oxygen [1]

$$FeS_2 + 7/2O_2 + H_2O \Leftrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

(2) Oxidation of ferrous iron Fe(II) (production of ferric iron Fe(III)). At low pH Fe the reaction rates strongly increased by microbial activity (e.g.,*Acidithiobacillus ferrooxidans).* Bacteria use the reaction as an energy-generating process, acting as a catalyze Fe^{2+} oxidation to Fe^{3+}, with rates 5 or 6 times higher than in sterile conditions, increasing acid generation. The soluble Fe^{3+} formed under these conditions, can effectively scavenge electrons from $S(^{-1})$ in pyrite, generating more Fe^{2+} once again, and this process is recycled. [1,2]

$$Fe^{2+} + 1/4O_2 + H^+ \Leftrightarrow Fe^{3+} + 1/2H_2O$$
$$FeS^{2+} 14\ Fe^{3+} + 8H_2O \Leftrightarrow 15\ Fe^{2+} + 2SO_4^{2-} + 16H^+$$

(3) Hydrolysis and precipitation of ferric complexes and minerals (f*erryhidrite, schwertmannite, goe*thite or jarosite) when the acid mine water, rich in ferric iron , reaches the surface. Most of the acid is produced at this stage [1].

$$Fe^{3+} + 3\ H_2O \Leftrightarrow Fe(OH)_3(s) + 3H^+$$

The development of a feasible, low cost and long-term inhibition of Fe2+ oxidation process at sulfide surface in solid waste accumulations could drive the mining industry towards a more sustainable future. Such technology should be focused on the understanding of the chemical and biological processes occurring on the surface of the sulphide minerals, as pyrite and pyrrhotite.

Different strategies to this problem have been proposed in the literature in the last years. Among them, the technologies designed to generate a physical barrier between pyrite surface and the oxidants agents seem to be the most promising techniques. Iron-phosphate or silicate coatings [3,4,5], complexation of ferric iron [6,7] and, more recently, the effect of lipids with two hydropobic tails on pyrite surface [8,9] prove to be effective in laboratory studies. All the techniques require the addition of specific chemical solutions to the waste rock as, phosphate or silicate rich solutions, H_2O_2, chemical complexing agent, lipids and organic solvents. However, none of these methodologies has been validated on field conditions mainly because of scale factor, which makes difficult to estimate the cost and environmental impact that these solutions may have.

Boojum Research LTD has been actively trying to address this problem since 1992, developing simultaneously laboratory (waste rock drums) and field tests (Inco, Buchans, Stanrock, etc) where natural phosphate rock (NPR), alone or combined with other

components (horse manure, straw, etc) was added to waste rock and tailings, respectively. This technology is proposed by this company has being suitable to groundwater and seepage treatment but, most of all, as a long-term AMD passivation technique.

Some parameters of this technology are not fully optimized but, field and lab demonstration tests have shown that a long-term inhibition technique may be possible due to the chemical properties of NPR plus the initiation of a biofilm coating on pyritic surfaces. However, the passivation mechanisms still need to be clarified in order to develop a final commercial product.

In this report we evaluate, for the first time, the surface of a complete set of rocks use by Boojum in two exposure periods of the Waste Rock Experiment (WRD) in order to gather more basic information for the passivation concept comprehension.

2. Waste Rock drum experience

The WRD experiment was initiated in 1992 to study the inhibition of pyrite corrosion by addition of (NPR) from Aurora Phosphate Mine (North Carolina) to waste rock. Different types of rocks, from the Selbaie Mine, a hypogene mineral deposit consisting of pyrite (FeS_2), sphalerite (Zn,Fe^{2+})S and chalcopyrite ($CuFeS_2$) in Northern Quebec, and with different pyrite grades, were used in these experiments. The waste rock was categorized on the mine site according to the standard waste rock disposal protocol (low pyrite, high pyrite and non-reactive, based on acid generating potential (AP) and neutralization potential (NP) evaluations.

The effects of NPR addition were tested in three main categories of applications of NPR and reported by Boojum in previous publications (see [10]). The materials used in the drums experience were:

- ***Low-pyrite fresh (Drum series A);***
- ***Low-pyrite old (Drum Series C)***
- ***High-pyrite fresh (Drum Series B).***

Each categorized material was divided into 3 different sets: **(1)** control; **(2)** NPR Layers add to WR; **(3)** NPR on top of WR and they were maintained inside 70L plastic containers equipped with a drain below a 20 cm Styrofoam pat at the bottom to ensure that none of the rock was immersed in water for any period of time. Each drum contained 61 to 78kg of rocks with a void ratio ranging from 41% to 48%. NPR was added at a ratio of 115kg NPR/t of waste rock (8.2kg per drum)

The waste rock was exposed outdoors in two different exposure periods (Figure 1 and 2). The first started in August 1992 and lasted until March 1995. During this period a total of 345L drained through each drum (this volume corresponds to rain water plus melting snow). Effluents were collected from each drum almost every month and pH, Eh, Conductivity and Acidity were measured. After this period, the drums were dismantled and the rocks stored indoors for 5 years. A second exposure period started in March 2000 and lasted until April 2001. During this period, no addition of NPR was to the drums and they were not drained, but kept on the Styrofoam supports. The accumulated rain water was drained completely from the drums after each rain and the same measurements as during the first exposure were made. Effluents were also taken to analysis and the total volume drained over the one year exposure was of 95L.

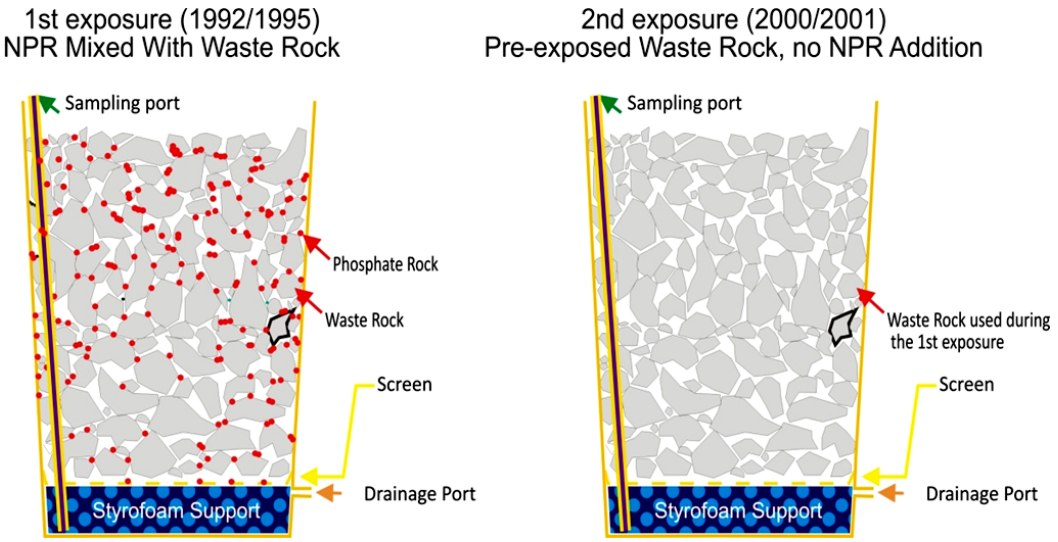


Figure 1 - WRD setup schematic

After approximately one year after the beginning of the first exposure experiment, all the controls samples started to produce an acidic effluent (pH below 3.5) in contrast to the NPR treated drums (Table 1). The pH measured on the NPR treated drums effluents was less variable and remained always above or close to pH 5. However, a different behavior was observed on drums series C, the waste rock collected after more than 4 years exposure on the waste rock pile, where a minimum pH of 3.35 was measured on the 3rd year of the experiment.

During the second exposure all drums, independently of their treatment, show a similar behavior. Within the first two measurements the pH values dropped in all drums. After day 2852 the pH rose again. The pH value in the controls drums was always slightly lower than in the treated drums.

A combination of biofilms, precipitates and NPR properties are the possible explanation to the passivation process and has been described by Boojum , a CRESTEC project at the University of Ottawa's and was confirmed by the AMIRA P933 project in 2006 [11].

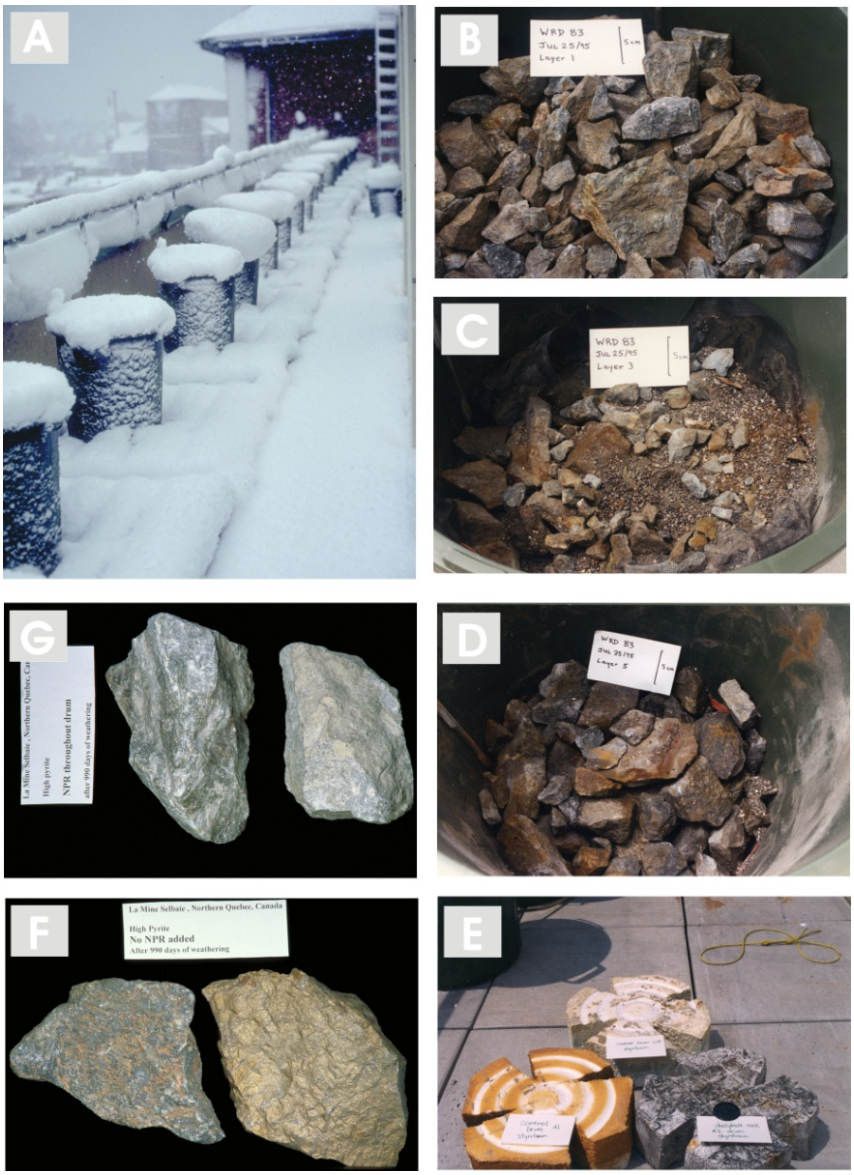


Figure 2 - (A) illustrates the set-up during the last winter of the first phase outdoors; (B) the top of a drum; (C), the NPR which collected on the mid-level window screen; (D) the phosphate on the screens at the bottom of the rock; (E) the Styrofoam supports a control drum containing no NPR (noticeably stained by iron hydroxide), a mixed-NPR drum (grey from particulates generated but not oxidized) and a waste rock control drum (nearly white) which was closed to the weather; (G), rocks from the high pyrite mixed treatment drum; and (F) high pyrite rocks from a non-treatment drum with a noticeably less shiny, pyritic surface than the rocks in 1b-G. [10]

Table 1 - WRD drums effluents pH during 1st and 2nd exposure monitoring periods

Day	A DRUM pH			B DRUMS pH			C DRUMS pH		
	Control	NPR Layer	NPR Top	Control	NPR Layer	NPR Top	Control	NPR Layer	NPR Top
0									
28	5.88	6.17	6.23	5.6	6.19	6.4	3.85	5.66	5.38
37	5.59	6.87	6.76	5.95	6.9	6.95	3.08	6.34	5.73
59	5.28	6.39	6.3	5.61	6.53	6.55	2.91	5.74	4.99
85	5.34	6.08	6.06	5.62	6.09	6.06	3.17	5.65	5.32
100	5.62	6.3	6.3	5.79	6.34	6.24	3.16	5.8	5.44
115	5.76	6.5	6.55	6.07	6.31	6.18	3.53	5.62	5.57
133	5.32	6.12	6.23	5.44	6.34	6.16	3.85	5.74	5.63
150	5.27	6.11	6.14	5.58	6.18	6.19	4.26	5.84	5.73
195	5.59	6.21	6.42	6.01	6.77	6.38	4.94	6.02	6.14
211	5.42	6.19	6.21	5.86	6.22	6.18	4.79	5.71	5.85
230	5.23	6.14	6.37	5.63	6.29	6.51	4.53	5.98	5.87
251	5.34	5.98	6.14	5.85	6.13	6.08	4.19	5.46	5.62
274	5.32	5.93	5.93	5.4	6.63	6.27	**3.11**	5.32	5.49
308	5.8	6.8	6.9	5.21	6.85	6.59		6.72	5.65
338									
358				**3.69**	5.98	6.02			
363				2.83	5.98	5.94	2.46	5.71	5.1
377	**3.03**	6.22	6.26	3.69	5.98	6.02			
421	2.87	5.74	6.05	2.83	5.69	5.81	2.74	4.61	4.43
462	2.87	5.54	5.78	2.82	5.64	5.76	2.81	4.69	4.51
543	3.26	5.72	6.05	3.36	5.76	5.92	3.21	5.39	4.93
574	3.67	5.78	5.81	3.37	5.32	5.68	3.11	5.15	4.73
604	4.89	6.87	6.91	4.05	6.85	6.66	3.24	6.59	6.31
646	3.96	5.21	5.39	3.69	5.23	5.54	3.04	6.05	
678	2.26	5.92	6.06	2.85	5.91	5.8	2.22	5.58	4.65
709	2.71	6.1	6.24	2.73	6.04	6.03	2.63	4.92	4.62
721	2.38	5.82	6.04	2.46	5.93	5.97	2.46	5.64	4.9
825	2.59	5.11	5.61	2.45	4.95		2.5	4.71	3.35
947	4.07	5.15	6.21	4.21		6.08	3.46	5.61	5.17
Storage period (5 YEARS)									
2758	4.22	5.16	5.38	4.13			3.73	4.75	
2810	3.31	5.02	5.7	4.24	4.95	4.72	3.86	4.18	3.98
2852	5.66	6.47	6.72	5.99	6.42	6.24	4.12	4.56	4.3
2864	5.31	6.23	6.58	5.82	6.5	6.38	4.03	4.57	4.31
2932	6.09	6.49	6.81	6.32	6.52	6.41	4.55	4.66	4.6
3145	6.06	6.49	6.82	6.03	6.28	6.04	4.65	5.2	5.49

3. Collaborative research

On March 2009, we started the observation of the 2nd exposure rocks , which were never observed under the SEM and the same is true for the unexposed rocks, which remained stored since 1999 indoors in plastic bags. Those rocks were never part of any of the previous projects, but the effluents were documented in [10]

Besides the observation of the above mentioned rocks, 1st exposure rocks were also used during this research in order to certify the previous identification of a biofilm coating

3.1 Inventory (rocks available at the U of T)

Rocks of both exposures are presently stored in the University of Toronto. The available rocks for the OCE project are listed below (Table 2).
Unexposed and 1st exposure (March 95) found were cut rocks samples. Most of the material from this period was sent to Australia (AMIRA project) and, therefore, there is a limited amount of samples for testing's and observations. We anticipate that they could be sending back and made available for the project if the need occurs.
The main material available for the OCE project are 2nd exposure samples (April 2001). Some samples weight more than 20 kg and can be used in future laboratory tests.

Table 2 - Waste rock inventory (March 2009, U of T)

		Number of Rocks		
	Drums	**Unexp.***	**1st Exp.**	**2nd exp.**
Series A	**A1**	5	5	111
	A2	3	11	105
	A3	2	6	7
	A4	4		10
Series B	**B1**	4	6	178
	B2	9	8	107
	B3	1	6	8
	B4	6		15
Series C	**C1**	4	1	24
	C2	4	8	110
	C3	2	10	9
	C4	4		7

*unexposed rocks have not been part of the first or second exposure experiment

4. Observation of Low pyrite rocks surfaces (Drum series A2);

Although the rocks used in these experiments came all from the Selbae mine, their surface heterogeneity, at a microscopic scale, was the major difficulty of this study which has conditioned the definition of an observation protocol. With the naked eye the surface

oxidation was generally not visible and surface patterns on the surface were not easy to identify.

Major surfaces differences could only be seen between unexposed and exposed surfaces, being the first more shinny and bright, with oxidation present only in small spots, while in the second's the surface is generally oxidized, which gives dark brown-green-grayish color to the rock, particularly, on those from the 2nd exposure period.

Both controls and NPR exposed rocks surfaces from the 2nd exposure period look very identical; although the NPR exposed rocks seem to have a more "dusty" surface, an observation already made during the dismantling of the rocks, as documented by Boojum **(Figure 3).**

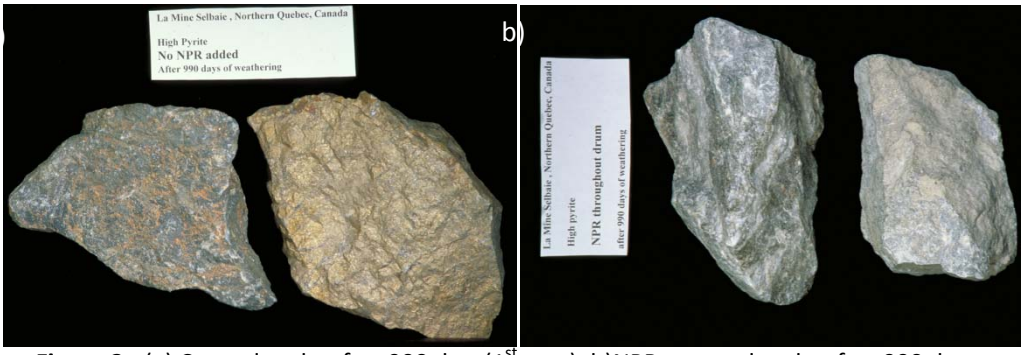


Figure 3 - (a) Control rocks after 900 days(1st exp.); b)NPR exposed rocks after 900 days.

In previous reports and publications, the biofilms were found in association with rocks from the A series drum. For that reason, we have selected to this preliminary report rocks from A1 (control) and A2 (NPR layer) for SEM/EDS survey.

It was made an effort to select 1st and 2nd exposed rocks with similar surfaces at a macroscopic scale but, unfortunately, no protocol could be optimized. Rocks were randomly selected from the available material and the surface observations were divided in two periods:

(1) 1st observation: the objective was to confirm the observations made on rocks from the 1st exposure period and gather preliminary information about unexposed and 2nd exposure rocks surfaces to establish a second observation target. The rocks used were only observed under a SEM and are shown below (Figure 4).

- **unexposed (1 rock)**
- **1st exposure (1 control; 1 NPR)**
- **2nd exposure (1 control; 1 NPR):**

(2) 2nd observation: the objective was to increase the information in order to establish a passivation process hypothesis for the second exposure period. To acquire more information the surfaces were observed in a binocular microscope and after in the SEM. The selected rocks are shown below (Figure 5). The size of the rocks selected for this observation period is relatively smaller than the rocks of the 1st observation. The reasons for their selection relates with (1) the fact that smaller surfaces are much easier to compare between rocks and the observations maybe more representative of the surface and (2) using smaller samples the preparation of the

rocks for SEM is easier because cutting can be avoid not only because matters of safety but also because is not so destructive.

- 2nd exposure (2 controls; 3 NPR)

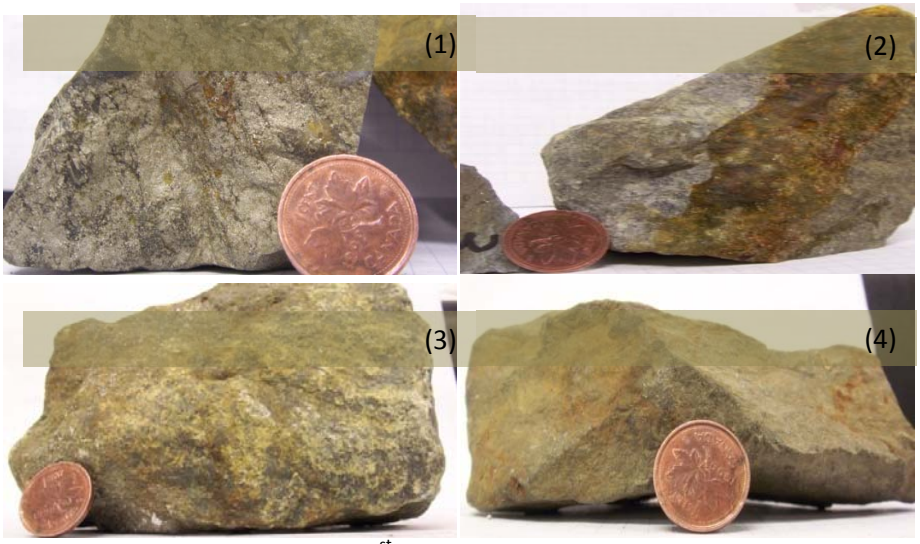


Figure 4 - Rocks used on the 1st observation survey: (1) unexposed; (2) NPR exposed 1st exp.; (3) Control 2nd Exposure; (4) NPR pre-exposed 2nd exp. There was also a control sample from the 1st exp (5). Period, but photo were not taken.

Figure 5 – (6) and (7) - A1 control rocks 2nd exposure; (8)(9) and (10) - A2 pre-exposed rocks 2nd exposure.

4.1. METHODS

A small section of each sample was cut (approximately 1 cm^3) and coated with a conducting metal (gold-palladium or carbon) for SEM observations. Gold coating was only applied on rocks from A2 2nd exposure (3 and 4) because of its intense interference with the S peaks. All other samples were coated 4 times with carbon.
SEM/EDS scans were made with a JSM-840 Scanning Microscope at the Geology Department of the University of Toronto.

5. SEM Surface observation - 1st assessment

5.1. Summary of observations

SEM scanning pictures obtained with a similar magnification of the rocks surfaces is shown below (Figure 6)

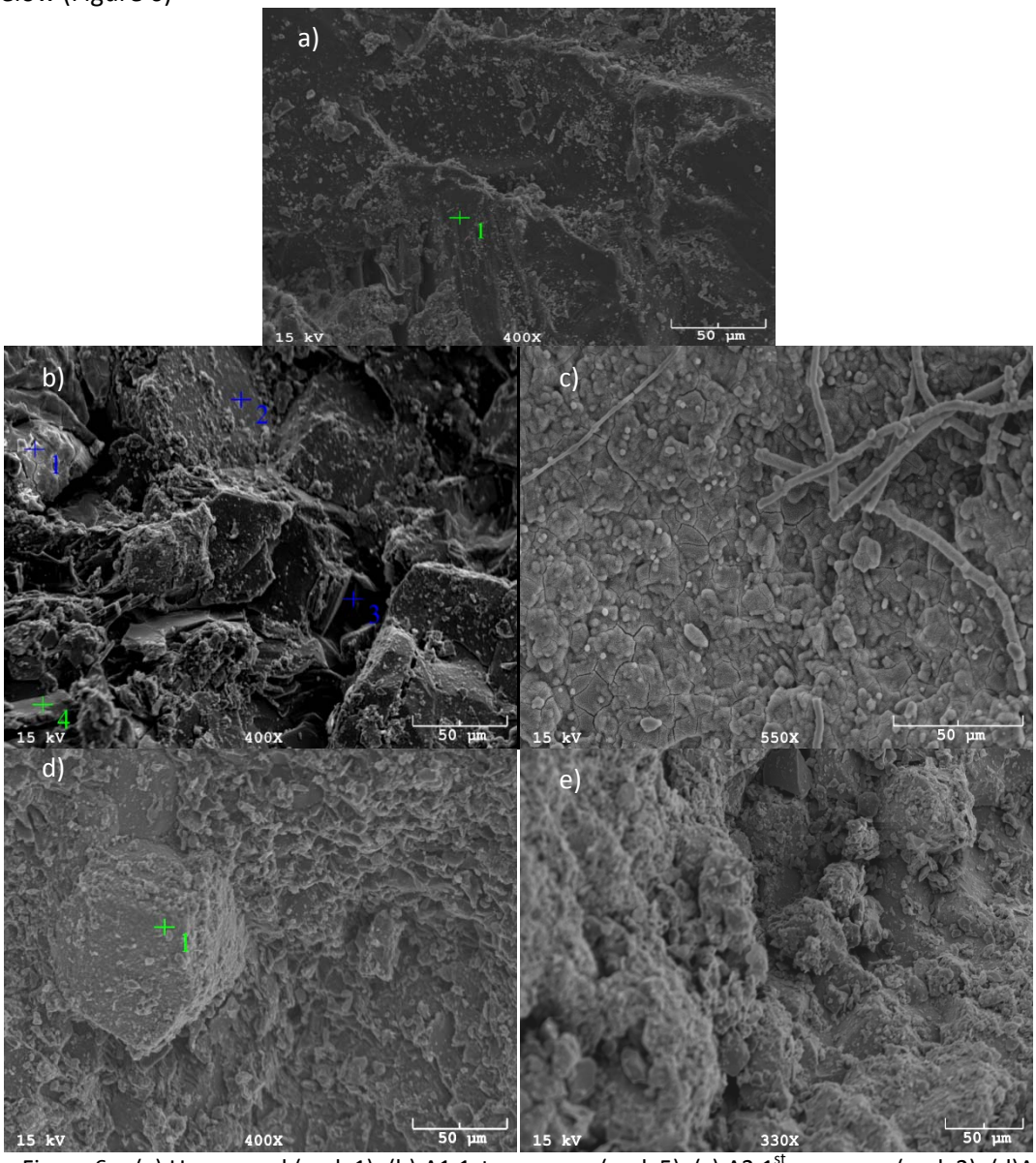


Figure 6 - (a) Unexposed (rock 1); (b) A1 1st exposure (rock 5), (c) A2 1st exposure (rock 2); (d)A1 2nd exposure (rock 3); (e) A2 2nd exposure (rock 4).

The major differences are observed in A2 1st exposure and they confirm what was already published by Boojum and identified also by AMIRA (see Figure 7).

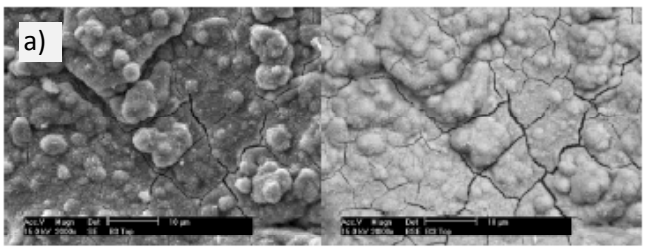


Figure 5.4.3.14 SEM images of iron hydroxide coating over the surface of B3 Top.

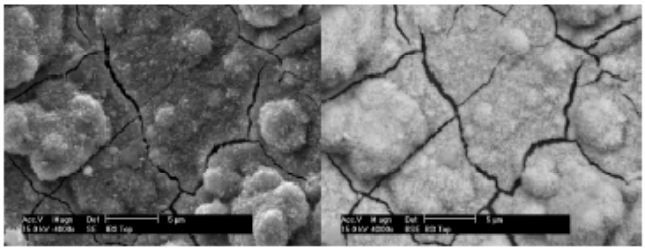
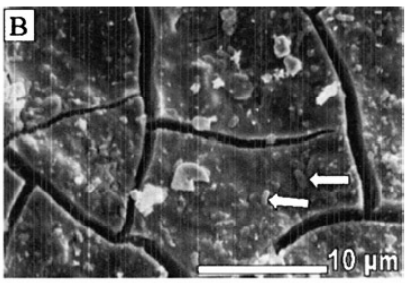


Figure 5.4.3.14 Continued.



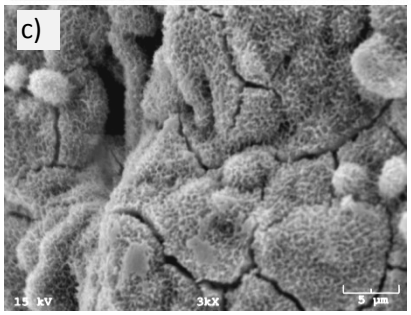


Figure 7 - (a) Amira P933/07: Drum B3; (b) Masato 2004: drums A3; (c) A2 Drum 2009 SEM (rock 2).

In AMIRA report [11] these findings are described as:

- All pyrite, coarse and fine, in all the A3 and B3 samples examined shows films 0.5 – 2 µm thick with some apparently attached and embedded fine particles (examples Figs. 5.4.3.1, 3, 4, 5, 7, 9, 15).

- These layers do not appear to be crystalline but gel-like covering almost all of the pyrite surfaces in conformal attachment (examples Figs. 5.4.3.6, 7, 10, 11,12, 15).
- Many cracks appear in these layers, suggesting hydration in formation of the layer material with subsequent dehydration in storage, from which the thickness of the layers can be estimated (Figs. 5.4.3.2, 3, 4, 7, 8, 10, 13, 14).

- Observations of pores through the gel-like layer are isolated but widespread (examples Figs. 5.4.3.1, 6, 11, 12).

- The observations of the thick gel layers with cracking (exfoliation) and pores in these NPR-addition samples constitute clear differences from the control thin sections.

- EDS analysis (1-10 µm depth) of elemental composition of the surface layers (Tables 5.4.3.1 – 3) finds a variety of particles and products including: iron sulphide with relatively low levels of oxidation (Figs. 5.4.3.1, 5); iron hydroxides (Fig. 5.4.3.14); iron sulfates (Figs. 5.4.3.3, 4, 7, 8, 9, 15); low levels of phosphate (Figs. 5.4.3.10, 11, 13, 15); minor Zn, Mg, Si, Al but not Ca which appears to be almost all in the gypsum.

- There is no obvious evidence of iron phosphate precipitate formation which has previously been suggested for the action of NPR addition in controlling pyrite oxidation. Ferris and Fyson previously investigated many of the exposed rocks in a search for iron phosphate precipitates with SEM/EDS methodology in a report to the

IRAP/NRC project. This also confirmed only rare occurrences of P on the surface of the rocks.

- However it should be clear that only small amounts of P at the mineral surfaces possibly below the detection limit of EDS, can stimulate microbial activity. Microbial activity in turn would lead to the conversion of inorganic P to organic P providing the basis for the generation of biofilm. It is likely that in the preparation of the samples all microbes were destroyed.

- These features are consistent with extensive microbial action and formation of exopolysaccharide biofilms, incorporating reaction products of the pyrite and other minerals, as described in detail in reviews such as "Methods for Study of Microbe-Mineral Interactions" (Eds. P.A. Maurice, L.A. Warren), Clay Mineral Society Workshop Lectures (Chantilly, VA, USA) (2006). Areas of biofilms from the NPR drums were reported by Kalin et al (Report 2; Appendix B) but these results make clear the extensive, almost full coverage of the pyrite in both the low- and high-pyrite wastes with NPR addition. A specific consequence of biofilm formation is the reduction of available oxygen beneath the layer, discussed in detail with measurements in Costerton et al, Biofilms, the Customised Microniche, J. Bacteriology, 2137 (1994) (Appendix A). As with the armouring discussion in Section 1.5, the parallel formation of jarositic and ferric hydroxide products at the surface, together with the high pH, will severely limit the available free ferric ion as the other oxidant. The reduction of both reactants appears to have effectively passivated the pyrite surfaces in the NPR drum experiments.

- The microbial action in the NPR drums contrasts with that normally associated with accelerated pyrite oxidation in the early stages of ARD where iron-oxidizing bacteria continually regenerate ferric ion oxidant. A reason for this can be seen in Figure 5.4.3.16 where the different type of microbial action likely to proliferate at higher pH is suggested. Differences in the microbial populations between the control and NPR addition drums will need to be established.

The surface composition of the A2 rock can also be compared with A3 rocks [12]. Besides the interference signal of the Gold-palladium coating, both spectra are very similar and the main elements are Fe, S and P but, in 2009 observation, in a much lower content (Figure 8)

The studied surface of A2 1st exposure rock is also cover by an extensively by fungal hypha (cylindrical shapes, see Figure 9) which maybe a newer colonization of the rock and not necessarily related with the passivation process. However they were already identified on 1995 by Masato, but those pictures were not published (see red binder).

On the 2nd exposure rocks the cracked surface wasn't found. Both control and A2 exposure rocks seem to have a similar surface with a high quantity of small fragments. EDS made in the surfaces show that Si, S, and Fe are the main components (Figures 10). These findings need to be further evaluated with more SEM/EDS scanning.

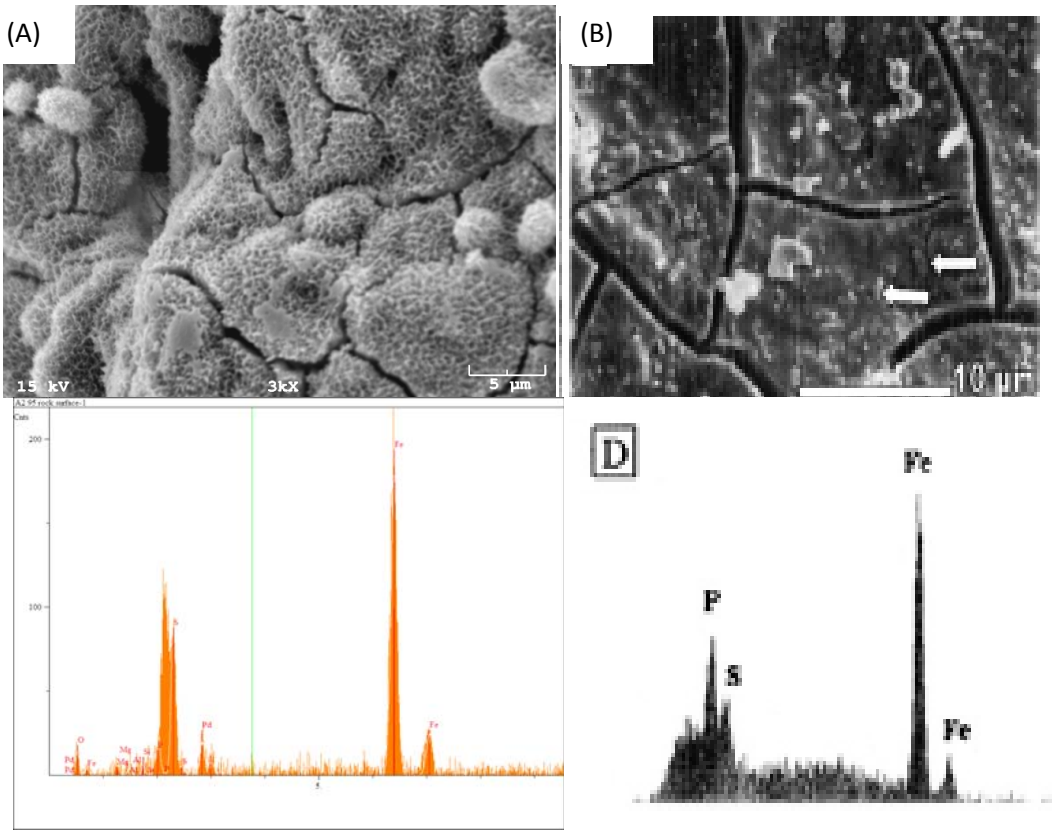


Figure 8 - (A) A2 SEM/EDS 2009 (rock 2); (B) A3 SEM/EDS 2004 [10]

5.2. Comments

The results of the preliminary SEM/EDS scanning seem to corroborate the previous findings. One of the significant observations is that the coating is still intact after 10 years of storage. The existence of a cracked surface, which is likely related to the biofilms previously identified, on the surface of A2 1st exposure was observed a highly dense distribution of Hyphas (fungi) .

This survey couldn't answer the question:

What happen on the 2nd exposure? Both the surfaces of control and exposed rocks seem very similar, but this corroborates the effluent characteristics and confirms that a coating developed. The initial two measurements of the second exposure could have resulted from rocks in the drums , which were not in the flow path of rain and hence unlikely in contact with the added NPR to the treated drums. Unfortunately, the rock exposure (skyward or downward , was not marked on the rocks during dismantling of the drums). However whatever initiated the biofilm formation with its associated coating is unclear but it appears to be a process with vigor.

EDS scans on most of the surfaces revealed Fe, S, and Si and to some extent Al, as the main components (See Appendix 1)- to some degree corroborating the findings of P933 on coating of pyrite with silica.

Could the passivation process be related with silicates?

During this trial only one surface of each exposure type of was observed, and that is the major limitation on this report on SEM/EDS findings. The SEM/EDS is a time consuming

process when looking to surfaces with a high topography as ours. The surface of the 1st exposed rocks seems, by now, that is already very well studied and we can be sure of our observations. The next steps should be focused on the 2nd exposure rocks from drum A2 and A1, to confirm this single observation.

All the SEM pictures taken during the 1st survey are given on APPENDIX 1.

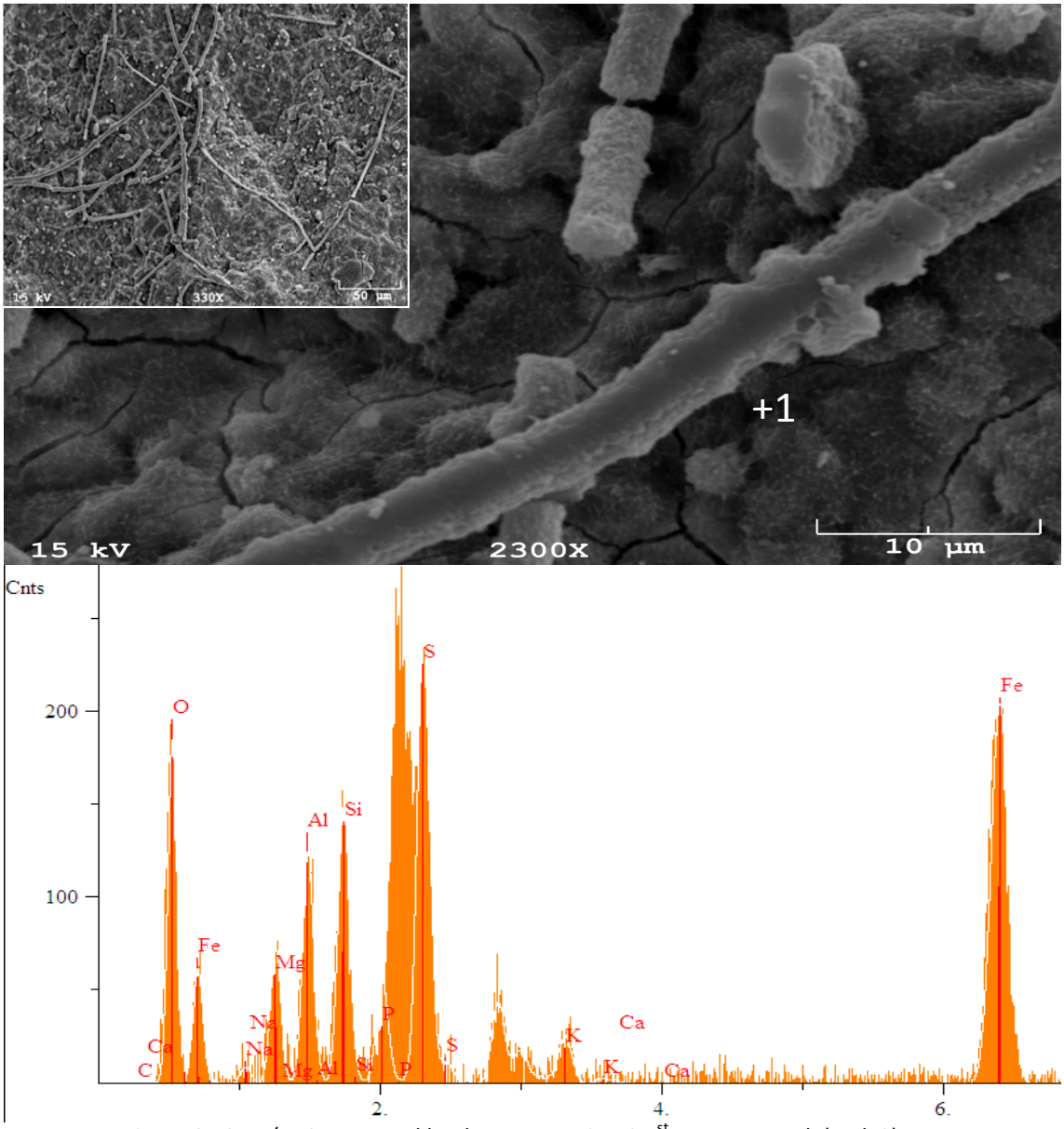


Figure 9 - SEM/EDS on Fungal hyphas present in A2 1st exposure rock (rock 2)

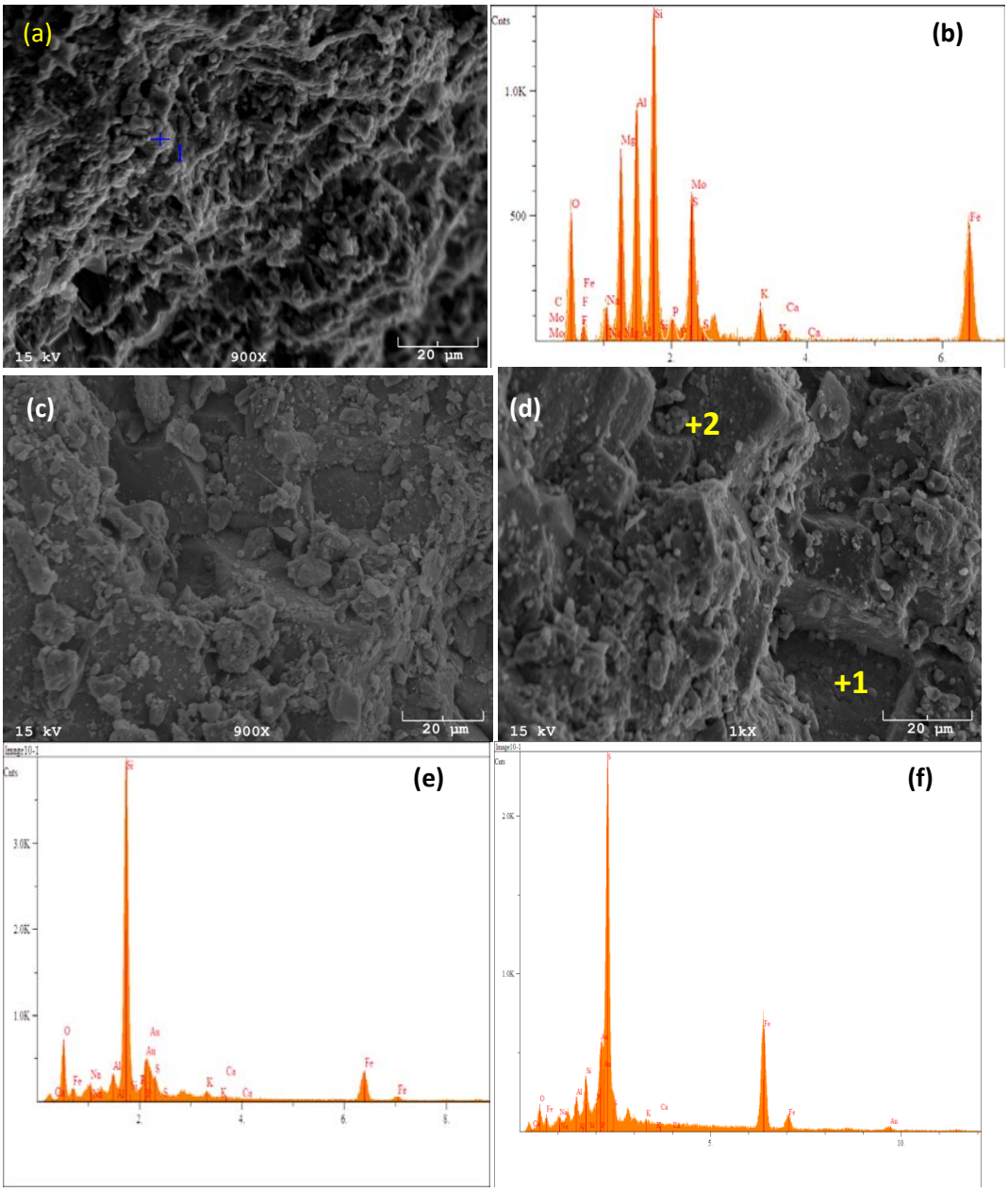


Figure 10 - (a) A1 (rock 3); (b)EDS of A1 Surface (rock 3) ; (c) A1 (rock 3) (d) A2 (rock 4).; (e and f) EDS scans on A2 (rock 4)

6. 2nd Survey: second exposure rocks

6.1. Rock surface observation

6.1.1. Binocular observations

The low pyrite rocks (A2) show a microcrystalline texture (sulphides, quartz) with some larger crystal of sulphide minerals (> 1mm). The macroscopic observation of the surface of NPR exposed rocks (8; 9 and 10) revealed that in these rocks, oxidation and precipitates are much more visible than in control rocks (6;7).

The surface of the NPR pre-exposed rocks is covered with red to brownish areas of oxidation (Figure 11), while in the controls rocks those areas are very scarce. Secondary precipitates (or evaporates) were also identified on the NPR exposed rocks surface, while in the control rocks they are only observed at higher magnification, between surface "valleys shapes".

No evidences of a biofilm layer could be observed at this scale.

A comparison between the rock surfaces, at different scales, is presented on Figure 12.

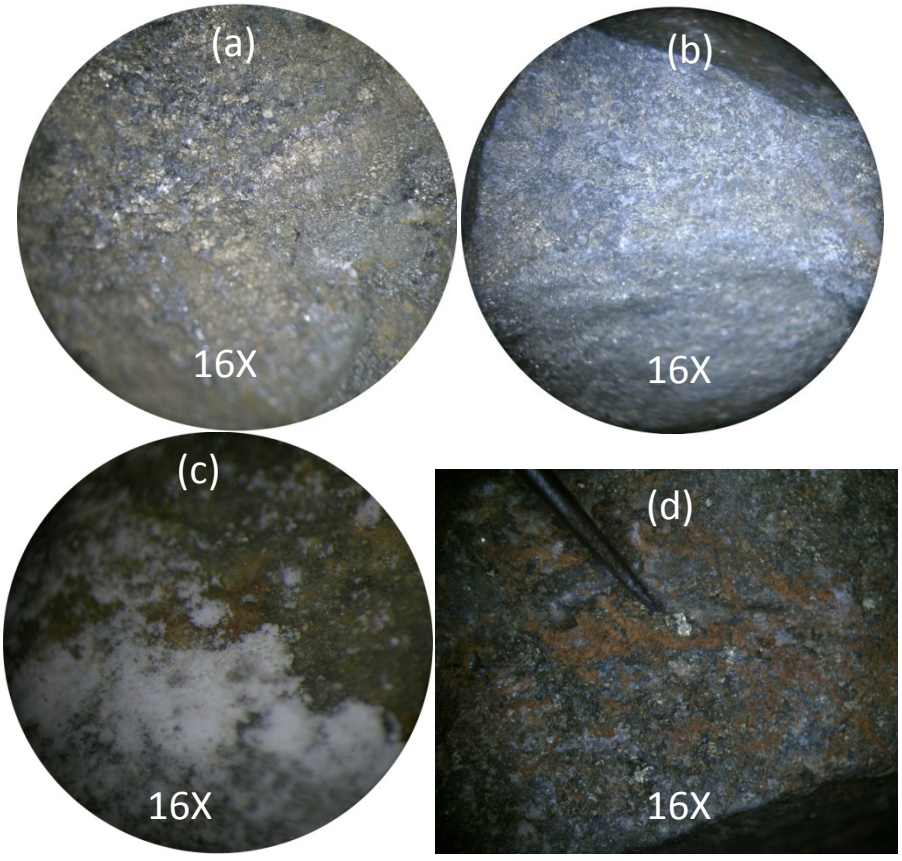


Figure 11- (a) and (b) Control rock; (c) Pre-Exposed rock (rock 8); (d) NPR exposed rock (rock 10)

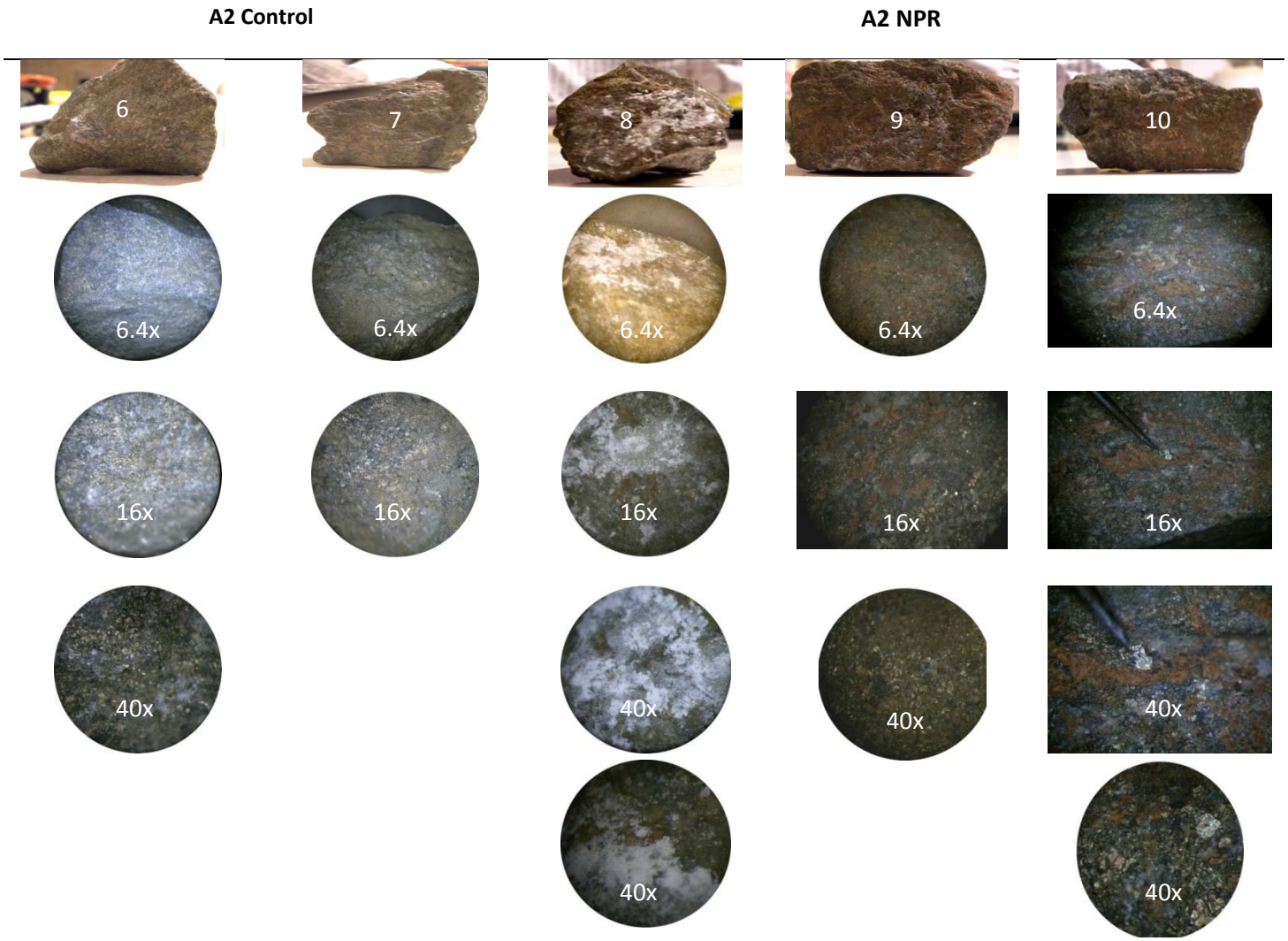


Figure 12 - Binocular microscope pictures.

6.2. Scanning Electron Microscope (SEM) observations

Summary

The 2nd survey confirmed the enormous heterogeneity of the rock surfaces, especially the ones previously exposed to NPR. The surface inspection revealed the following:

- Fe, S and Si are the most abundant elements at the surface of both sets. However, coatings and biofilm related structures (crack surface, exfoliation,)were only identified on the NPR pre-exposed rocks (Figure 13a and d);
- There is no evidence of phosphates on the surface;
- Observation of Secondary precipitates or evaporites on the surface of NPR pre exposed rocks with Mg, Si and Al.(Figure 13b and f)
- Fragments of amorphous silicates (???) seem to be abundant , particularly, on control rocks surfaces (Figure 13c and d)
- The surface of pyrite on the exposed rocks is covered with a more dense matrix composed by a mixture of precipitates and small mineral fragments, while in the control, only small fragments could be identified. (Figure 13 e and f)

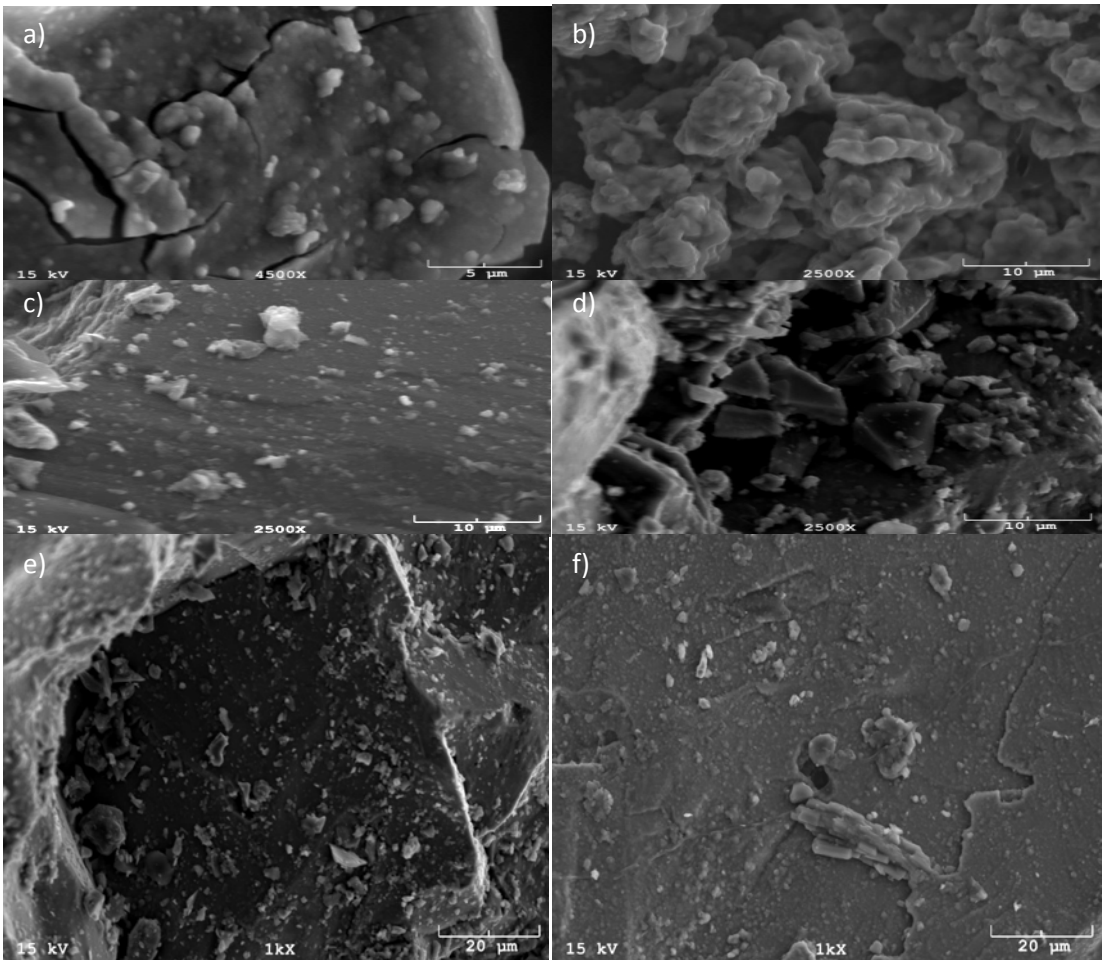


Figure 13 – Comparison of SEM observations (a) Rock 9; (b) rock 8; (c) Rock 7; (d) rock 6; (e) rock 6

A comparison of the rocks surfaces, at same scale, is presented in Figure 14. All pictures taken during this survey are given in Appendix 2.

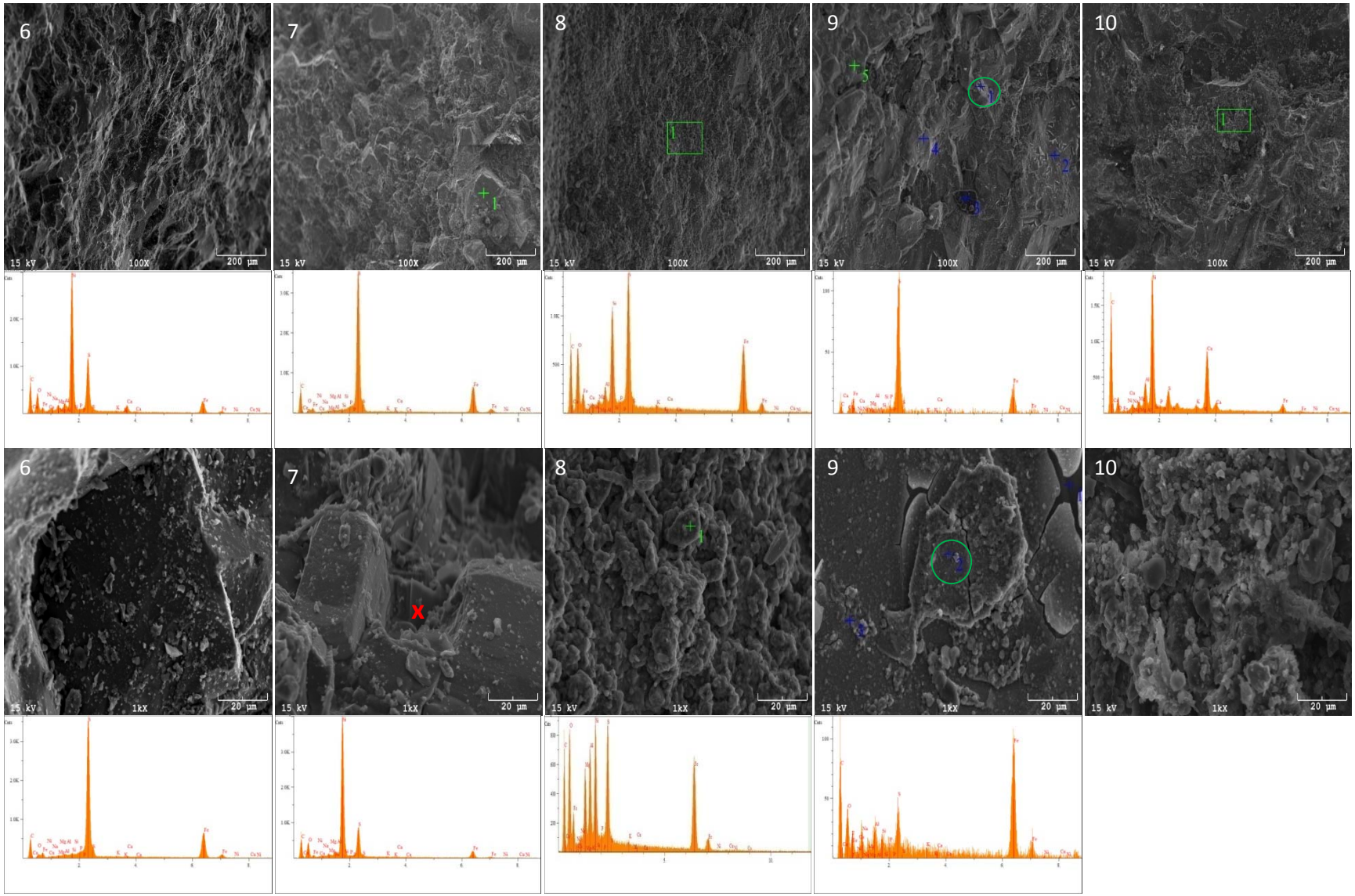


Figure 14 – Comparison and EDS of rock surfaces at different magnifications (x100) and (x1000).

7. Conclusion

Pyrite Oxidation: Mechanisms of Passivation hypothesis

In the previous research of the WRD rocks surfaces a biofilm was identified on the pyritic rocks treated with NPR. Most studies show that the presence of phosphate in solution significantly reduce the oxidation rate of pyrite at pH values equal to or greater than 4 and that above this value, phosphate became irreversibly bound to an Fe^{3+} bearing product on the pyrite surface during the oxidation process [3, 4, 13]**.** In Boojum experiments**,** instead of an iron-phosphate coating, little or none phosphorus was found at the surface and the effluents pH were always above 4.

In this report we describe the surfaces of control and NPR exposed rock from the 1st exposure period. The biofilm cracked surface was only identified on the NPR exposed rock (Rock 2) while the control surface shows an irregular cover by small and fine precipitates. These features are also in agreement with what was observed in 1995 (see red binder). Beside Fe and S, Si is the most common element at the surface. An XRD of the surface will be required to identify which minerals are related to these elements.

The differences between surfaces and effluents led to the conclusion that the passivation mechanism was due to the physical barrier provided by the biofilm which decreased the pyrite reactivity with air and water. The effluents of the 1st exposure period seem to corroborate these findings as well as the identification of this biofilm by different researchers [11,12]. However, none of these researchers established the exact connection between NPR, the biofilm and what contribution does it has for biofilm initiation.

The most feasible hypothesis seems to be that NPR, due to its chemistry and solubility characteristics, acts as a nutrient source to bacteria. This hypothesis can be extrapolated from the work of Masato et al [12]. which has successfully revived the biofilm in a nutrient solution demonstrating the importance of the essential nutrient to growth and survival of the coating biofilm.

Boojum Research LTD has studied the NPR dissolution (*i.e.* decant cycles) and showed that NPR dissolution and elements release occurs within an acidic environment (H_2SO_4 0.1N) but not in the presence of water(Figure 15a). **Chi et al (2007)** [14, 15]made the same observation when studying the reaction mechanism of bioleaching phosphorus from NPR (chemical composition similar to Boojum NPR) in presence of pyrite and autotrophic bacteria *Acidithiobacillus ferrooxidans,* an abundant acidophilic species in sulphide deposits (Figure 15b).

According to these authors, NPR is leached and dissolved due to pyrite bio-oxidation of *A.ferrooxidans* with production of H_2SO_4 and $FeSO_4$ and forms soluble phosphorus compounds [14]. Iron (II) from the $FeSO_4$ is oxidized to $Fe^{3+,}$ producing energy for the growth of *A.ferrooxidans,* generating more acid solution (Equation 1 to 5).

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2H_2SO_4 + 2\,FeSO_4 \quad \textbf{(1)}$$

$$2H_2SO_4 + 4FeSO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad \textbf{(2)}$$

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S \quad \textbf{(3)}$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad \textbf{(4)}$$

$$3H_2SO_4 + Ca_3(PO_4)_2 \rightarrow 3CaSO_4 + 2H_3PO_4 \quad \textbf{(5)}$$

(a)

NPR Composition		Sulphuric Acid		Distilled water	
g/10g of NPR		DC 0 - 8 stirred	1L Non stirred	DC 10 stirred	1L Non stirred
		Grams released from NPR			
P	0.840	0.451	0.490	0.010	0.011
K	0.015	0.011	0.009	0.001	0.001
Ca	2,788	0.731	0.680	0.510	0.450
Mg	0.033	0.033	0.031	0.001	0.001

(b)

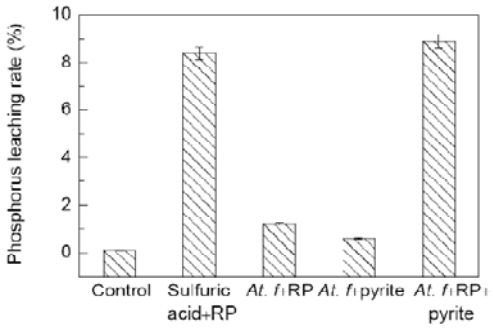


Figure 15 – (a)Release of macronutrients from NPR after Decant Cycles with H2SO4 0.1N and distilled water; (b) NPR Phosphorous bioleaching rate [13]

The dissolution test made by Boojum revealed that is not only P (inorganic) that solubilizes but also other essential nutrients as Ca, K and Mg (table 3) and, therefore, the NPR in the waste rock drums may be more complex.

With the exception of carbon and nitrogen, the elements released from the NPR during the decant cycles belong to those that are commonly required in a microbial growth media. Macro-elements as phosphorus (nucleic acids synthesis, ATP), potassium (enzymes activation), calcium (cells walls and endospores), magnesium (ribossomes, nucleic acid and cell membranes) and the micronutrients iron (electron transport systems), manganese, copper, nickel, molybdenum, cobalt and zinc (components of protein complexes and enzyme activators) are utilized by microbes in their metabolic processes and being released from NPR they become available as nutrients for the organism. [16]

Plus, the growth and propagation of other microorganisms on pyrite surface (fungi, ..) may have been enhanced by the improving chemical conditions within the waste rock, as result of calcium buffering capacity (which may be the reason for the high pH observed on the drum effluents).

Water and temperature are other requirement to the biofilm growth. Rainwater carried the NPR particles trough the drum, into the pyrite surfaces were the reaction occurs. Then, water and solutes were transported through the fracture/pores of WR. The importance of the size of the NPR particles is not yet addressed and, therefore, we cannot make any assumptions.

Temperatures within the waste rock pile can be as high as 70ºC and below 0ºC, which could limit the survival of some species and benefit others. However, the identification of the biofilm bacteria species was not made and so; we cannot elaborate a detailed description of the biofilm structure and growth. The bacteria community study could give us a better understanding of biomineralization processes.

Assuming the process described above, Boojum proposed coating technology differs from others [3,4] because phosphate is not added as a soluble form to co-precipitates with iron oxide and also because it doesn't require the addition of H_2O_2 as an extra oxidant, which doesn't seem very realistic as a field technique [13,17]. Another advantage of this methodology seems to be the biofilm longevity and the ability to be revived after long storage periods (simulation of dryness), a positive aspect in long-term assessment.

But, if this interpretation seems to be valid to understand the 1st exposure passivation mechanism, the same correlation cannot be made to the 2nd exposure rocks. The observations made on 2nd exposure rocks do not resemble the structure identified in the previous exposure period and, so, the passivation may be the result of a different reaction. Moreover, all effluents monitorized in each drum (control and pre-treated rocks) showed a similar passivation trend, although no NPR was added at this stage.

Precipitates are much more abundant on 2nd exposure rock surfaces, especially on NPR pre-exposed rocks, rather than on the 1st exposure rocks. White and red precipitates were observed with binocular microscope (Figure 16)

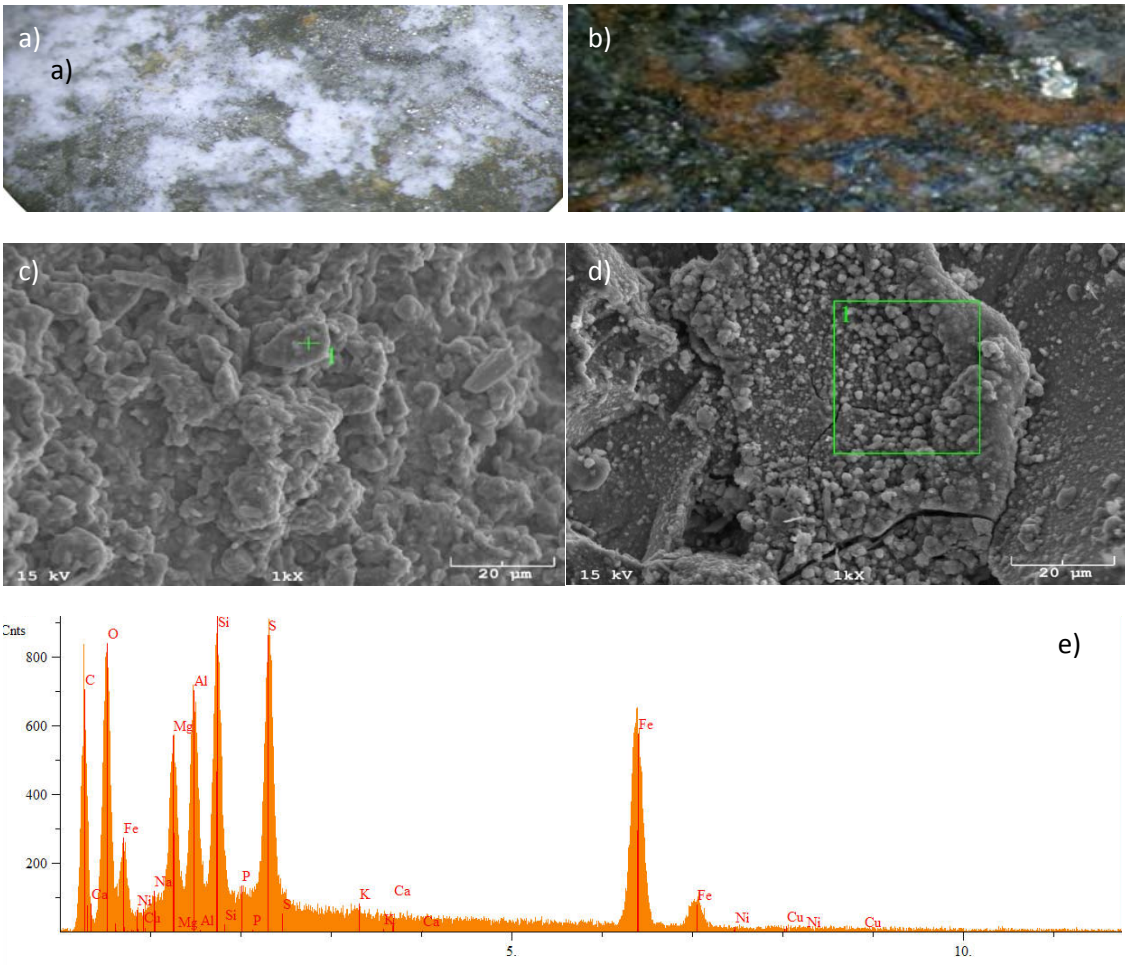


Figure 16 – (a) Evaporites (Rock 8); (b) Fe-hydroxides(???) (rock 10); (c) Evaporites SEM; (d) Fe-hydroxides SEM; (e) Figure 16c EDS.

The acidity generated in the beginning of the 2nd exposure monitoring period may have dissolve minerals and mobilize elements and, in their pathway through the drum, they reacted with acid-neutralizing agents such as carbonates and silicates. As the pH increased, the precipitation of metal-bearing oxyhydroxide and oxyhydroxide sulfate minerals (red precipitates) occur, removing some of the dissolved metals from the water. These secondary minerals act in a certain pH range as buffers so that a sequence of pH buffering reactions can be observed in the tailings environment [1].

	A DRUM			B DRUMS			C DRUMS		
	pH			pH			pH		
Day	Control	NPR Layer	NPR Top	Control	NPR Layer	NPR Top	Control	NPR Layer	NPR Top
2758	4.22	5.16	5.38	4.13			3.73	4.75	
2810	3.31	5.02	5.7	4.24	4.95	4.72	3.86	4.18	3.98
2852	5.66	6.47	6.72	5.99	6.42	6.24	4.12	4.56	4.3
2864	5.31	6.23	6.58	5.82	6.5	6.38	4.03	4.57	4.31
2932	6.09	6.49	6.81	6.32	6.52	6.41	4.55	4.66	4.6
3145	6.06	6.49	6.82	6.03	6.28	6.04	4.65	5.2	5.49

As a result of neutralization, the precipitation of metal hydroxides or hydroxide sulfates is favored, as gibbsite, amorphous $Al(OH)_3$, amorphous $Fe(OH)_3$,ferrihydrite, goethite, or schwertmannite. The dissolution of most aluminosilicate minerals also consumes H+ ions and contribute base cations (Ca, Mg, Fe(II)), alkali elements (Na, K) and dissolved Si and Al to the tailing pore water, which could explain the abundant amorphous silica on the surface of control and exposed rocks. [11]

Acidophilic microorganisms affect silicates solubilization and, by increasing Si concentration, acid consumption and, consequently, $Fe3^+$ precipitates as iron hydroxyl compounds (most commonly jarosites) that reduce the availability of $Fe3^+$ for leaching and cause passivation of the sulfide mineral and release of trace elements that may inhibit microorganisms. At. ferrooxidans is responsible for the production of amorphous silicates in an acidic mine tailings environment suggesting a role in Si cycling. [18].

More information about these precipitation and passivation reactions is given on **Appendix 3**

FUTURE RESEARCH

The passivation mechanism observed on the 1st exposure rocks seems to be strictly linked with the biofilm formation. However, the importance of NPR and what factors seem to initiate this process are still unknown. It is also important, to definitely validate NPR as a valid technique, optimizing all the operational parameters (rates, long-term assessments, etc.).

As discussed with Margarete Kalin, the proof of concept will be dependent of what can be observed on the rock surface, what reactions occur and how they influence the biofilm initiation. Therefore, the following approach has been suggested:

1) **Single rocks**
   a) Total surface area and sulphide minerals surface area – determination of reactive surfaces (this methodology is not defined yet. Limitation: high topography of the surface)
   b) Reactivity of rocks – immersion of control and exposed rocks (2nd exposure) in water. Measurement of elements release (organic/inorganic), pH, conductivity, etc. ***(to be improved)***

2) **NPR**
   a) NPR solution and NPR Particles: In a decant funnel, put 1 to 0.5 kg of NPR New/unused (Figure 17). Drain water and sulphuric acid (pH =3) through the funnel. Measure pH and conductivity. The solution should be analyzed with ICP. Determinations of particles mesh size. ***(to be improved, as it may not work for particles)***

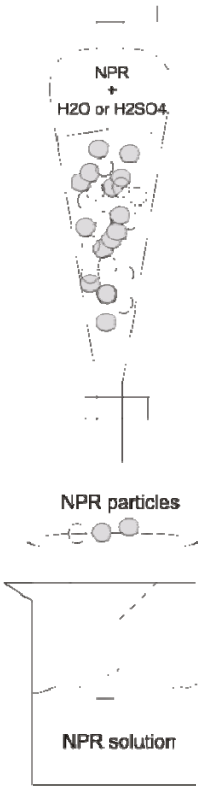


Figure 17 - Decant NPR tests

3) **Columns test**

a) New column/drums experiences taking into account three different scenarios: (Figure 18)

   I. Waste pile - NPR on Top (NPR before WR pile) - this setup intends to simulate the disposal of NPR on the new waste rock piles layers. Rain water (distilled water) passing through the NPR will transport particles, without dissolution (pH>3), to the waste rock container. NPR particles and solution should be monitorized (suggestion: after 1, 2, 4, 8, 16, 24 hours, and then daily)

II. Waste pile - NPR mix with waste rock – this setup intends to simulate the mixture of NPR and waste rocks. The final effluent should be monitorized.

III. Seepage – this setup has 2 functions: (a) control – Rainwater passing through WR and generating ARD; and (b) ARD passing through NPR drum simulating seepage treatment before biopolishing. ARD and the final effluent should be monitorized.

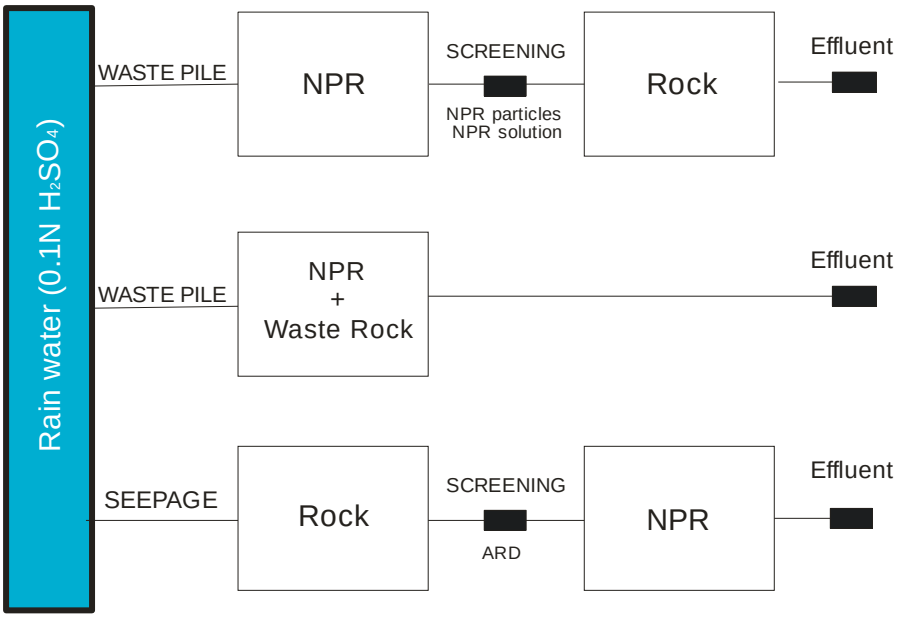


Figure 18 – Proposed Scheme for column test

REFERENCES

[1] Dold, B. (2005) - "Mineralogía, geoquímica y geomicrobiología para el manejo ambiental de desechos mineros" XXIV Curso Latinoamericano de Metalogenia UNESCO-SEG.

[2] Konhauser, K. (2007) – "Introduction to Geomicrobiology"Blackwell Science, 425pp

[3] Belzile, N.; Maki, S. , Chen, Y. and Goldsack, D. (1997)- "Inhibition of pyrite oxidation by surface treatment". Science of The Total Environment, Volume 196, Issue 2, 177-186p

[4] Z. J. Georgopoulou, K. Fytas, H. Soto and B. Evangelou (1996) "Feasibility and cost of creating an iron-phosphate coating on pyrrhotite to prevent oxidation" Environmental Geology.Volume 28, Number 2, 61-69p.

[5] Kargbo, D (2005) – "Stability of Silicate Coatings on Pyrite Surfaces in a Low pH Environment". Journal of Environmental Engineering, Vol. 131, No. 9,

[6] Khummalaia, N. and Boonamnuayvitayab, V (2005) –"Suppression of arsenopyrite surface oxidation by sol-gel coatings". Journal of Bioscience and Bioengineering.Volume 99, Issue 3, 277-284p.

[7] Y. Lan, X. Huang and B. Deng (2002) – "Suppression of Pyrite Oxidation by Iron 8-Hydroxyquinoline" Archives of Environmental Contamination and Toxicology Volume 43, Number 2.

[8] Elsetinow, A.; Bordab,M ; Schoonen, M; Strongin, D (2003) – "Suppression of pyrite oxidation in acidic aqueous environments using lipids having two hydrophobic tails". Advances in Environmental Research, Volume 7, Issue 4, 969-974p

[9] Kargbo, D; George Atallah, G and Chatterjee, S (2004) "Inhibition of Pyrite Oxidation by a Phospholipid in the Presence of Silicate". Environ. Sci. Technol., , 38 (12), pp 3432–3441

[10]Kalin, M.; Harris,B. (2005). "Chemical precipitation within pyritic waste rock" Hydrometallurgy 78, pp 209-225).

[11] AMIRA P933 Reports 2007 (in Boojum Database)

[12] Ueshima;M; Danielle Fortin;D and Kalin, M (2004) – "Development of Iron-Phosphate Biofilms on Pyritic Mine Waste Rock Surfaces Previously Treated with Natural Phosphate Rocks". Geomicrobiology Journal, 1521-0529, Volume 21, Issue 5, 313 – 323pp

[13] Elsetinow, A.; Schoonen, M; Strongin, D. (2001). Aqueous geochemical and surface science investigation of the effect of phosphate on pyrite oxidation . Environmental science & technology. 2001, vol. 35, n°11, pp. 2252-2257

[14] CHI Ru-an, XIAO Chun-qiao, HUANG Xiao-hui, WANG Cun-wen; WU Yuan-xin (2007)- "A Novel Approach to Bioleach Soluble Phosphorus from Rock Phosphate". The Chinese Journal of Process Engineering. Vol 7, Nº2.

[15] CHI Ru-an, XIAO Chun-qiao, HUANG Xiao-hui, WANG Cun-wen; WU Yuan-xin Chi et al (2007) Bio-decomposition of rock phosphate containing pyrites by Acidithiobacillus ferrooxidans. J. Cent. South Univ. Technol. (2007)

[16] (Chapelle, F; (1993) - “Ground-Water Microbiology & Geochemistry” John Wiley & Sons, Inc).

[17] The National Academies Press (2002) - “Evolutionary and Revolutionary Technologies for Mining”. Committee on Technologies for the Mining Industry, Committee on Earth Resources, National Research Council.

[18] Dopson,M; Halinen, A; Rahunen, N. Boström, D. Sundkvist, Riekkola-Vanhanen,M; Kaksonen, A; Puhakka, J (2008) “Silicate mineral dissolution during heap bioleaching”. Biotechnology and bioengineering. 99(4):811-20.

Other information

Formation of Silica Deposits on Mars by Acid Weathering: Physical-Chemical Constraints

McAdam, A. C.; Zolotov, M. Y.; Mironenko, M. V.; Sharp, T. G.

American Geophysical Union, Fall Meeting 2007, abstract #P11A-0255

Many chemical and mineralogical characteristics of martian surface materials are indicative of exposure to acidic solutions. Silica-rich outcrops and soils found in Gusev crater could also result from acid weathering. We used thermo chemical equilibrium and coupled kinetic-thermodynamic models to investigate conditions under which abundant amorphous silica forms by low-temperature (273 K) H2SO4-HCl acid weathering of mafic/ultramafic rocks. We explored the effects of pH, solution/rock ratio (W/R) and rock composition on secondary mineralogy, solution chemistry, and timing of weathering. Modeling shows that silica-rich deposits form mainly under very acid conditions (pHs<~2-3) and at high W/R ratios (~102-103). High W/R ratios may represent solution discharge in spring environments, groundwater flow, or lake settings. If solution pH does not change much during high W/R alteration, silica-rich (>90 vol% silica) mineral assemblages form at pHs<~2. If acid solutions with original pH<~2 are neutralized as weathering proceeds, abundant silica precipitates at early stages of weathering (W/Rs >~102) below pH ~3. Calculated timing of silica deposition is consistent with these inferences. Kinetic models also demonstrate that silica can dissolve when the solution neutralizes. Silica precipitation conditions are similar for several potential martian protoliths, however, the volume precipitated increases with increasing rock SiO2 content (Shergotty basalt > Adirondack olivine basalt > Chassigny dunite). Low-pH deposition of amorphous silica is consistent with experimental Mars analog studies and theoretical models directed at understanding martian acid weathering. Observed Ti enrichment in some of the high silica deposits in Gusev crater is also consistent with a low-pH process. Rapid dissolution of mafic minerals and glass in cold, low-pH fluids could have been followed by the precipitation of silica and Ti-oxide owing to their low and comparable solubilities in these solutions. However, a high-temperature (e.g., hydrothermal) origin for the observed deposits remains a possibility.